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Professor Arthur W. Sleight 63218C
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Department of Chemistry
Oregon State University
Corvallis, Oregon 97331-4003 AFOSR-TR-95
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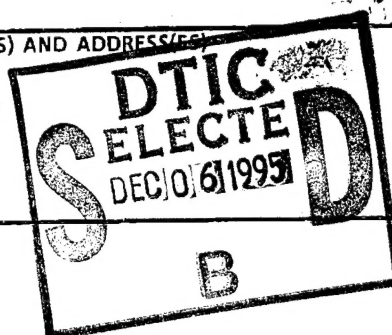
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One of the areas we investigated for new superconductors is reduced oxides of niobium. One unusual synthesis approach to prepare these materials has been ion exchange reactions and another has been quenching reactions from very high temperatures.

Many reduced niobium oxides in A-Nb-O ternary systems where A is an alkaline or alkaline earth metal have been reported. Some examples are LiNbO₂ (1), NaNb₁₀O₁₈ (2), BaNb₈O₁₄ (3), Ba₂Nb₁₅O₃₂ (4) and Ca_{0.75}Nb₃O₆ (5). Some of strongly reduced niobates contain a [Nb₆O₁₂]O₆ cluster with metal-metal bonding as found in NaNb₁₀O₁₈ (2), BaNb₈O₁₄ (3), Ba₂Nb₁₅O₃₂ (4) and Rb₄Al₂Nb₃₆O₇₀ (6). These cluster compounds seemed like particularly good candidates in view of the known superconducting Mo-S cluster compounds. Furthermore, it was reported that LiNbO₂ changed from a semiconductor to a superconductor with a T_c = 4.5 K by deintercalation of Li⁺ ions (7). This confirms the potential for superconductivity in reduced niobates. Recently, we discovered a new reduced rubidium niobium oxide, Rb_{1.51}Nb₁₀O₁₇, with a layered structure and having a [Nb₆O₁₂]O₆ cluster (8). This compound is not superconducting down to 4.2 K, but changing the electron concentration in the cluster seemed like a worthwhile goal. The Rb⁺ ions occupying the interlayer space appeared to be good candidates for deintercalation or ion exchange reactions.

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Exploratory Synthesis Employing Unusual Synthesis Approaches

Arthur W. Sleight
Department of Chemistry
Oregon State University
Corvallis, Oregon 97331-4003

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Introduction

One of the areas we investigated for new superconductors is reduced oxides of niobium. One unusual synthesis approach to prepare these materials has been ion exchange reactions and another has been quenching reactions from very high temperatures.

Many reduced niobium oxides in A-Nb-O ternary systems where A is an alkaline or alkaline earth metal have been reported. Some examples are LiNbO_2 (1), $\text{NaNb}_{10}\text{O}_{18}$ (2), $\text{BaNb}_8\text{O}_{14}$ (3), $\text{Ba}_2\text{Nb}_{15}\text{O}_{32}$ (4) and $\text{Ca}_{0.75}\text{Nb}_3\text{O}_6$ (5). Some of strongly reduced niobates contain a $[\text{Nb}_6\text{O}_{12}]\text{O}_6$ cluster with metal-metal bonding as found in $\text{NaNb}_{10}\text{O}_{18}$ (2), $\text{BaNb}_8\text{O}_{14}$ (3), $\text{Ba}_2\text{Nb}_{15}\text{O}_{32}$ (4) and $\text{Rb}_4\text{Al}_2\text{Nb}_3\text{O}_{70}$ (6). These cluster compounds seemed like particularly good candidates in view of the known superconducting Mo-S cluster compounds. Furthermore, it was reported that LiNbO_2 changed from a semiconductor to a superconductor with a $T_c = 4.5$ K by deintercalation of Li^+ ions (7). This confirms the potential for superconductivity in reduced niobates. Recently, we discovered a new reduced rubidium niobium oxide, $\text{Rb}_{1.51}\text{Nb}_{10}\text{O}_{17}$, with a layered structure and having a $[\text{Nb}_6\text{O}_{12}]\text{O}_6$ cluster (8). This compound is not superconducting down to 4.2 K, but changing the electron concentration in the cluster seemed like a worthwhile goal. The Rb^+ ions occupying the interlayer space appeared to be good candidates for deintercalation or ion exchange reactions.

Cluster Compounds

Powder samples of $\text{Rb}_{1.51}\text{Nb}_{10}\text{O}_{17}$ were obtained by heating a mixture of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ (9) and Nb powder with the molar ratio 1:14 in an evacuated quartz tube at 1050°C for 12 hr. Powder of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ was prepared by heating a stoichiometric mixture of Rb_2CO_3 and Nb_2O_5 at 1000°C for 15 hr. The products always contained a small amount of NbO and NbO_2 . The hexagonal lattice constants for the powder sample are $a = 6.021(2)$ and $c = 38.90(1)\text{\AA}$, agreeing well with those reported (8) for a single crystal ($a = 6.020(1)$ and $c = 38.703(8)\text{\AA}$).

Ion-exchange reactions were performed with various alkali chloride and HCl solutions. Deintercalation reactions were performed with aqueous KMnO_4 solution and with I_2 or Br_2 solutions in acetonitrile. The reaction temperature ranged from room temperature to 180°C . For reactions above 100°C , an autoclave (70ml) with a teflon lining was used as a reaction vessel. The reaction duration was 1-10 days. The solid products were separated by centrifuging, washed with distilled water or acetonitrile, and dried at 50°C .

The products were identified by X-ray powder diffraction using $\text{CuK}\alpha$ radiation. Lattice constants were determined by using silicon as an internal standard. Products were completely decomposed by a concentrated HCl solution under hydrothermal conditions at 180°C for 15 hr to yield a white amorphous powder which crystallized to Nb_2O_5 at elevated temperatures. After filtration, the amount of alkali in the solution was analyzed by atomic absorption spectroscopy.

Neither ion-exchanged nor deintercalation was detected below 100°C. However under hydrothermal conditions above 100°C, rubidium ions could be partially ion-exchanged and deintercalated. The starting material was completely oxidized to white amorphous powder in concentrated acid at temperatures above about 150°C. The X-ray powder patterns for ion-exchanged and deintercalated compounds are indexed with hexagonal cells similar to that of the starting material, and their lattice constants are slightly changed when compared with those of the starting material. This fact suggests that the crystal structure of products remains intact during this soft-chemical reaction. TG curves and gas evolution curves were measured in a He atmosphere and in air for the Li⁺ and K⁺ ion-exchanged compounds. Weight gain caused by oxidation of niobium is observed above about 300°C in the TG curves for the ion-exchanged and deintercalated compounds measured in air; whereas in He atmosphere, no weight gains are observed. A large evolution of H₂O gas up to about 150°C and small continuous one up to about 500°C are observed for all the ion-exchanged compounds. A distinct H₂O evolution at about 400°C is observed for the H⁺, Li⁺ and Cs⁺ ion-exchanged compounds. No gas evolution is observed for the deintercalated compound. **Table 1** shows chemical composition, lattice constants and weight changes for the ion-exchanged and deintercalated compounds. The amount of H₂O was estimated from the weight loss of TG curves measured in He atmosphere.

The maximum replacement of Rb⁺ ions was observed for the compound ion-exchanged with K⁺ ions at 180°C for 5 days. The sum of rubidium and other alkali ions for all the alkali ion-exchanged compounds is less than the amount of rubidium ion (1.51) in the starting material. Two explanations were considered. Either niobium is oxidized with a decrease of cations in the interlayer space or protons are incorporated to maintain the niobium oxidation state during the ion-exchange reaction. The latter explanation appears more likely partly because of the distinct evolution of H₂O at about 400°C for the H⁺, Li⁺ and Cs⁺ ion-exchanged compounds. This water is thought to be formed by protons and oxygen atoms of the host lattice, such protons being incorporated into the niobate during the ion-exchange reactions with alkaline ions. For the Na⁺ and K⁺ ion-exchanged compounds, no distinct evolution of H₂O gas is observed at about 400°C. Instead, there is a gradual weight loss and small continuous evolution of H₂O gas up to about 500°C, following to the removal of water in the interlayer space. This suggests that the Na⁺ and K⁺ ion-exchanged compounds also incorporate protons during the ion-exchange reaction. The weight gain observed in TG curves measured in air is always smaller than the calculated one, assuming no oxidation. The niobium in the ion-exchanged compounds may be partially oxidized during the ion-exchange reactions. However, the change of oxidation state of niobium during soft-chemical reaction cannot be precisely estimated because of the NbO and NbO₂ impurities in the reactant ion exchanged.

TABLE 1
**Chemical composition, lattice constants and weight changes for Rb_{1.51}Nb₁₀O₁₇,
ion-exchanged and deintercalated compounds**

Chemical composition	a (Å)	c (Å)	(1)	(2)	(3)
Rb _{1.51} Nb ₁₀ O ₁₇	6.021(2)	38.90(1)		9.74	10.53
Rb _{0.25} H _{1.25} Nb ₁₀ O ₁₇ ·0.8H ₂ O	5.970(8)	40.62(5)	2.09	8.12	8.43
Li _{0.67} Rb _{0.31} H _{0.53} Nb ₁₀ O ₁₇ ·0.8H ₂ O	6.005(8)	40.77(5)	1.58	8.94	9.35
Na _{0.86} Rb _{0.28} H _{0.37} Nb ₁₀ O ₁₇ ·2.5H ₂ O	6.007(9)	40.73(5)	3.69	3.91	6.88
K _{1.02} Rb _{0.02} H _{0.47} Nb ₁₀ O ₁₇ ·0.9H ₂ O	5.998(7)	40.98(6)	1.62	7.97	9.20
Cs _{0.44} Rb _{0.48} H _{0.59} Nb ₁₀ O ₁₇ ·0.8H ₂ O	5.996(8)	40.78(6)	1.54	5.99	8.79
Rb _{0.15} Nb ₁₀ O ₁₇	6.018(2)	39.16(2)		8.70	10.64

(1) Weight loss(%) measured in He atmosphere.

(2) Total weight gain(%) measured in air.

(3) Calculated total weight gain(%).

Mass spectrometry shows no gas evolution for the deintercalated compounds, indicating the reduced negative charge on the niobate layer is compensated only by the Rb⁺ ions in the interlayer space. Deintercalation proceeds to Rb_{0.15}Nb₁₀O₁₇ when treated with 0.21M Br₂ acetonitrile solution at 120°C for 7 days. As seen in **Table 1**, the lattice constants of the oxidized products change only slightly during the deintercalation. During deintercalation of layered AMO₂ oxides (A = alkali metals and M = transition metals), a more significant increase in the lattice spacing perpendicular to the layers is frequently noted and is attributed to increased repulsion between these layers. Because the niobium ions in the NbO₆ octahedra and the NbO₄ tetrahedra are presumably in the fully oxidized +5 state, oxidation during deintercalation only occurs in the [Nb₆O₁₂]O₆ cluster. This cluster is shielded from the region of alkali cations by the NbO₆ octahedra and the NbO₄ tetrahedra. This may partly explain the smallness of the expansion along the *c* axis. The formal oxidation state of Nb in the octahedral Nb₆ cluster is calculated to increase from 2.08 to 2.31 during deintercalation. This oxidation of the cluster is expected to change interatomic distance within the cluster, and cluster orientation may also change. These factors will also influence the lattice parameters of the product of deintercalation.

The a.c. susceptibility of materials prepared was examined down to 4.2 K using a Lakeshore AC Susceptometer. No evidence of superconductivity in our products of ion-exchanging or deintercalating Rb_{1.51}Nb₁₀O₁₇ was observed down to 4.2 K. The Rb⁺ ions in the reduced niobium oxide Rb_{1.51}Nb₁₀O₁₇ were partially ion-exchanged by other alkali ions. Simultaneous incorporation of protons occurred. Deintercalation of Rb_{1.51}Nb₁₀O₁₇ with a Br₂ solution in acetonitrile at

120°C yielded $\text{Rb}_{0.15}\text{Nb}_{10}\text{O}_{17}$. Unlike the case of LiNbO_2 , this deintercalation reaction does not lead to a product showing superconductivity above 4.2 K.

High Temperature Synthesis

A Brew furnace was used to achieve temperatures as high as 2000°C followed by rapid quenching to room temperature. This was a highly exploratory approach seeking entirely new compounds that might be superconducting or have other interesting properties. Systems investigated were Mg/Nb/O , Ca/Nb/O , Sr/Nb/O , Ba/Nb/O , Al/Nb/O , Cr/Nb/O , Ti/Nb/O , La/Nb/O , Ce/Nb/O , Sc/Nb/O , and Y/Nb/O . Syntheses were conducted in high vacuum to insure reducing conditions. No new superconducting phases were discovered.

Miscellaneous Incomplete Results

Superconductivity was recently discovered at low temperatures in SrRuO_3 . This suggests that other oxides containing Ru should be investigated for possible superconductivity. New phases were prepared which contain Ba, Ru, O, and either W, Mo, V, or Cr. We continue to investigate the structure and properties of these new compounds. In related work, we have for the first time grown crystals of BaPtO_3 .

Superconductivity occurs in the BaBiO_3 - KBiO_3 solid solution. The compound LiBiO_3 was not previously known, but we have now prepared it using hydrothermal conditions. The structure has been determined and found to be completely different than that of KBiO_3 .

REFERENCES

1. G. Meyer and R. Hoppe, *J. Less-Common Metals*, **46**, 55 (1976).
2. J. Köhler and A. Simon, *Z. Anorg. Allg. Chem.*, **572**, 7 (1989).
3. S. J. Hibble, A.K. Cheetham, J. Köhler and A. Simon, *J. Less-Common Metals*, **154**, 271 (1989).
4. B. Hessen, S. A. Sunshine, T. Siegrist, A. T. Fiory and J. V. Waszczak, *Chem. Mater.*, **3**, 528 (1991).
5. S. J. Hibble, A. K. Cheetham, D. E. Cox, *Inorg. Chem.*, **26**, 2389 (1987).
6. M. J. Geselbracht and A. M. Stacy, *J. Solid State Chem.*, **110**, 1 (1994).
7. M. J. Geselbracht, T. J. Richardson and A. M. Stacy, *Nature*, **345**, 324 (1990).
8. N. Kumada, N. Kinomura, R. Wang and A. W. Sleight, *Mater. Res. Bull.*, **29**, 41 (1994).
9. G. D. Fallon and B. M. Gatehouse, *J. Solid State Chem.*, **22**, 405 (1977).
10. N. Kumada, S. Muramatsu, F. Muto, N. Kinomura, S. Kikkawa and M. Koizumi, *J. Solid State Chem.*, **73**, 33 (1988).

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